



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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SHORT ABSTRACT

The overall aim of the present study is to focus on the melt processing and rheology of poly (lactic acid) (PLA) and its efficacy towards the fabrication of recyclable bionanocomposite and its end use application as a biolubricant and biodiesel additive. PLA is known to have poor melt strength, which is a major limitation for melt processing and recycling using the conversional technologies. In this thesis, melt stabilization of PLA has been attained through melt extrusion with thermally stable and crystalline silk.

Over the assessment, the impact of silk nanocrystals (SNC) on melt degradation of PLA during thermomechanical process is investigated at melting temperatures (185 °C and 200 °C) under shear (40 and 100 rpm). The rate of degradation is studied through the estimation of molecular weight distribution at different residence times (up to 30 min) using gel permeation chromatography (GPC). Simplified two-parameter model which accounts for degradation and recombination is used to predict the kinetic parameters by coupling with Arrhenius equation. The impact of SNC and processing condition on macromolecular change of PLA matrix is also investigated using melt rheology. The incorporation of SNC in PLA matrix is observed to hinder the melt degradation which is confirmed by the increment in degradation activation energy and reduction in degradation rate constant. FTIR results confirm the formation of weak interaction between the SNC and PLA, which can be considered to be the reason for the stabilizing effect of SNC. The morphology of the SNC-PLA composite captured by field emission scanning electron microscope (FESEM) shows network formation, which is absent in neat PLA (NPLA) matrix. Crystallinity is improved and the reduction in number average molecular weight (M_n) and weight average molecular weight (M_w) with increasing residence time is minimized as compared to pristine PLA.

The recyclability performance of neat PLA (NPLA) and SNC-PLA is also studied through the essential investigations on melt rheology, solution viscosity and thermal degradation behavior under repetitive extrusion at high shear and temperature. The presence of SNCs is observed to facilitate the crystallization process and delay the thermal degradation of PLA matrix. This led to the reduction in cold crystallization peak temperature with lower crystallization half-time and higher growth rate. The substantial improvement in nucleation density observed through Polarized Optical Microscope (POM) proves the nucleating effect of SNC in all processing cycles. Moreover, the rheological investigation (complex viscosity, storage and loss modulus values) revealed the stabilizing effect of SNC and the drastic degradation of pristine PLA in third and fourth cycle is observed to be fortified by the presence of SNC. Cole-Cole plot and cross over frequencies have been correlated with the molar mass distribution of NPLA and SNC-PLA

bionanocomposite during processing, which is further supported by the intrinsic viscosity measurement and acid value analysis.

On the other hand, stable onset degradation temperature is obtained for SNC-PLA bionanocomposite ($T_5\% \sim 334$ °C) as compared to NPLA, which is drastically reduced from 336 °C (first cycle) to 322 °C (fifth cycle). The activation energies are estimated using isoconversional methods (Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO)). Stable activation energy values (~ 130 kJ/mol) are obtained for SNC-PLA bionanocomposite at three consecutive extrusion cycles whereas, in case of NPLA, these values significantly reduce from ~ 150 kJ/mol (first cycle) to ~ 110 kJ/mol (second cycle). Nelder-Mead simplex method is used to optimize the kinetic parameters of nucleation and growth model (A2), which is observed as the best fit of experimental thermogravimetric analysis (TGA) data. Decomposition products are analyzed by thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TGA-FTIR).

Reactive extrusion is also performed to have branched, crosslinked and SNC grafted chain topology of PLA, with different levels of gel percentage by adding small amount of radical initiator (dicumyl peroxide (DCP)). Grafting of SNCs on PLA macromolecules provide remarkable improvement on rheological and thermal properties, which is confirmed by $^1\text{H NMR}$ and FTIR investigation. Significant improvement observed on zero shear viscosities and the crossover point shifts to lower frequencies as compared to branched and crosslinked PLA system. Along with SNC grafting, the crystallization behavior is also enhanced with the formation of stable and uniform crystals during cooling, which leads to a single melting peak. The rate of crystallization of PLA is improved but the percentage crystallinity is decreased with increasing DCP fraction as higher grafting and subsequent crosslinking restricts the macromolecular movements, which is essential for crystallization process. Furthermore, SNC grafting improves the reprocessability performance of PLA and provides improved rheological properties as compared to the branched and crosslinked PLA at all reprocessing cycles.

Subsequently, two other recycling alternatives are introduced in this research for the first time to utilize recycled and waste melt processed PLA and its lower molecular weight oligomers. The first part demonstrates the dissolution of melt processed PLA in lactic acid/water mixture which is blended with soybean oil (SO) to be tested as a biolubricant. Dynamic viscosity and Viscosity-Temperature dependency of the blend is investigated at temperature of 25 °C, 40 °C, 60 °C, 80 °C and 100 °C. Promising results are obtained for 30/70 and 50/50 blend of soybean oil and recycled PLA. The second part highlights the recycling of low molecular weight PLA (oligomer) into biodiesel additives. Four different molecular weight oligomers (500 Da,

1000 Da, 1500 Da and 2000 Da) are synthesized using microwave reactor and dissolved in soybean oil based methyl ester in different concentrations (3, 5, 10 and 25 g/L). The impact of PLA-oligomer on the cold flow properties (cloud point, pour point and dynamic viscosity) are investigated using rheometer and optical polarimetry as per ASTM standards. Furthermore, engine performance and exhaust gas analysis are performed using Kirloskar TV-1 engine. The cloud point and pour point decreases respectively by 6 °C and 2 °C with remarkable viscosity reduction at lower temperature, which improves the exhaust gas characteristic.